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MERCURY REMOVAL AGENT AND MANUFACTURING METHOD OF SAME

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[There are no amendments to this patent.]

Abstract

Objective

The objective of this invention is to provide a type of agent for removing mercury and mercury compounds in flue gas as well as its manufacturing method.

Constitution

A type of agent for removing mercury in combustion flue gas characterized by the fact that it is prepared by adding water to an inorganic powder with a large specific surface area, such as silicon dioxide, titanium dioxide, active terra alba, silica gel, molecular sieves, and diatomaceous earth, or a mixture of diatomaceous earth and pearlite, followed by agitation and then reaction with a solution prepared by adding an alcohol to dissolve a silane coupling agent having γ-mercapto groups.

Claims

1. A type of agent for removing mercury in combustion flue gas, characterized by the fact that it is prepared by reaction between an inorganic powder having a large specific surface area and a silane coupling agent having γ-mercapto groups at its terminals.

2. A type of agent for removing mercury in combustion flue gas, characterized by the fact that it is prepared by reaction between diatomaceous earth or a mixture of diatomaceous earth and pearlite having a large specific surface area and a silane coupling agent having γ-mercapto groups at its terminals.

3. A method for manufacturing an agent for removing mercury in combustion flue gas, characterized by the fact that it is prepared by adding water to an inorganic powder with a large specific surface area, followed by agitation and then reaction with a solution prepared by adding an alcohol to a silane coupling agent having γ-mercapto groups and agitating the mixture for dissolution.

Detailed explanation of the invention

[0001]

Industrial application field

This invention pertains to a type of agent for removing mercury (mercury and mercury compounds) in the flue gas of municipal trash incinerators, industrial waste incinerators, sewage incinerators, and other combustion devices, and its manufacturing method.

[0002]

Prior art

In the prior art, the agents for removing mercury and mercury compounds (mercury removal agent, hereinafter) in combustion flue gas include wet removal agents and dry removal agents. The following is a brief account of these types of mercury removal agents.

[0003]

(1) Wet removal agent: This type of removal agent is an aqueous solution prepared from a potassium permanganate-sulfuric acid mixed solution, hypochlorous acid-Table salt solution, thiourea, sodium sulfide, sodium thiosulfate, etc. By means of gas-liquid contact, mercury in the gas is transferred to the liquid.

[0004]

(2) Dry removal agent: This type of removal agent has sulfur or a sulfur compound, a metal that can form an amalgam with mercury or halide of said metal [sic], etc., supported on activated carbon, or an inorganic carrier. As this type of removal agent makes contact with the gas containing mercury, mercury is trapped and removed. The removal agent is usually contained in a fixed-bed reactor or mobile-bed reactor for use.

[0005]

Problems to be solved by the invention

For conventional wet removal agents, it is necessary to treat wastewater containing mercury. This is undesirable.

[0006]

On the other hand, for conventional dry removal agents, there are the following problems.

(1) Conventional dry removal agents usually have poor heat resistance, and are deactivated or decompose at 120°C or higher. Consequently, it is difficult to use this type of mercury removal agent in various incinerators that require withstanding a temperature of 150-230°C.

[0007]

(2) Conventional dry removal agents that have good heat resistance usually have a mercury removal rate as low as 30% or lower. This is undesirable.

[0008]

(3) In consideration of the performance, it is necessary to increase the contact area between the removal agent and gas. Consequently, for the dry removal method using a conventional dry removal agent, the device of course is large.

[0009]

(4) It is necessary to perform an operation to replace the removal agent before the mercury concentration at the outlet of the reactor exceeds the tolerance levels, and to have the equipment for said operation.

[0010]

(5) Most of the components of the removal agent is the carrier component. When it is used without recycling, the cost is high. On the other hand, when it is recycled, it is necessary to have equipment for desorption and recovery of mercury.

[0011]

The objective of this invention is to solve the aforementioned problems of the wet and dry removal agents of the prior art by providing a type of dry or semidry agent for removing mercury and mercury compounds in flue gas, and its manufacturing method.

[0012]

Means to solve the problems

This invention provides a type of mercury removal agent and its manufacturing method with the following features.

(1) A type of agent for removing mercury in combustion flue gas characterized by the fact that it is prepared by reaction between an inorganic powder having a large specific surface area react and a silane coupling agent having γ-mercapto groups at its terminals.

[0013]

(2) A type of agent for removing mercury in combustion flue gas characterized by the fact that it is prepared by reaction between diatomaceous earth or a mixture of diatomaceous earth and pearlite having a large specific surface area react and a silane coupling agent having γ-mercapto groups at its terminals.

[0014]

(3) A method for manufacturing an agent for removing mercury in combustion flue gas characterized by the fact that it is prepared by adding water to an inorganic powder with a large specific surface area, followed by agitation and then reaction with a solution prepared by adding an alcohol to a silane coupling agent having γ-mercapto groups and agitating the mixture for dissolution.

[0015]

Examples of the inorganic powder with a large specific surface area for use in this invention include silicon dioxide, titanium dioxide, active terra alba, silica gel, molecular sieves, diatomaceous earth, and a mixture of diatomaceous earth and pearlite. In particular, when a mixture of diatomaceous earth and pearlite is used, the preferalba ratio by weight of diatomaceous earth:pearlite is in the range of 10/0:7/3.

[0016]

Examples of silane coupling agents having γ-mercapto groups include γ-mercaptopropyltrimethoxysilane and γ-mercaptopropylmethyldimethoxysilane.

[0017]

The amount of the silane coupling agent having γ-mercapto groups with respect to the inorganic powder for use in the reaction should be in the range of 0.1-5 wt%, or preferably in the range of 0.1-1 wt%. When said silane coupling agent containing γ-mercapto groups is reacted with the inorganic powder, it is preferred that said silane coupling agent be hydrolyzed to the silanol form (silanolation), and a condensation reaction be performed with the hydroxyl groups present on the surface of the inorganic powder to form siloxane bonds. It is preferred that when silanolation is performed, the silane coupling agent having ?-mercapto groups be agitated and dissolved in an alcohol.

[0018]

When the dry mercury removal agent of this invention is manufactured, an inorganic powder having a large specific surface area is dispersed in water. Then, a solution prepared by adding alcohol to the silane coupling agent having γ-mercapto groups, followed by agitation for dissolution and silanolation, is added to said dispersion, and the mixture is agitated for reaction, followed by drying and crushing to obtain the dry mercury removal agent. In said method, when drying and crushing are not performed, a slurry-like mercury removal agent (semidry mercury removal agent) can be obtained.

[0019]

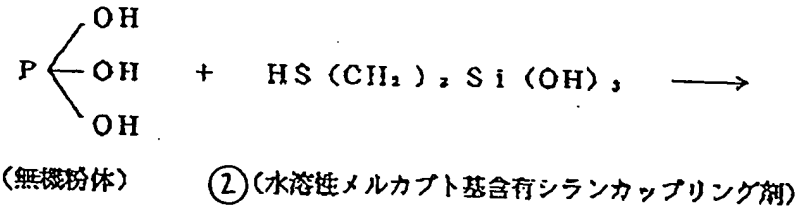
Operation

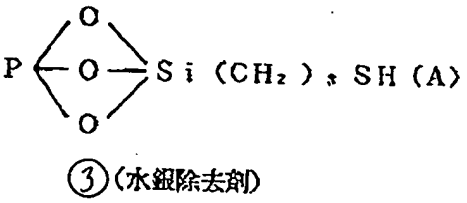
(1) Reaction between inorganic powder and water-soluble silane coupling agent containing γ-mercapto groups

Usually, on the surface of inorganic powder (P), many active hydroxyl groups are present. A condensation reaction takes place between the active hydroxyl groups and said

water-soluble silane coupling agent containing γ-mercapto groups, so that silane is introduced onto the surface of the inorganic powder.

[Structure 1]



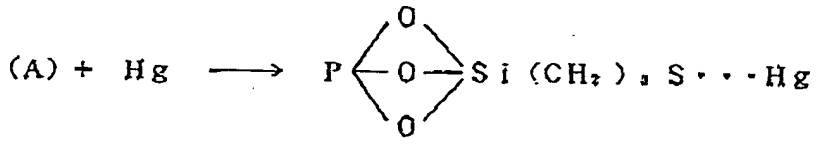


Key: 1 (Inorganic powder)
2 (Water-soluble silane coupling agent containing mercapto groups)
3 (Mercury removal agent)

[0020]

(2) Removal of mercury using said mercury removal agent (A)

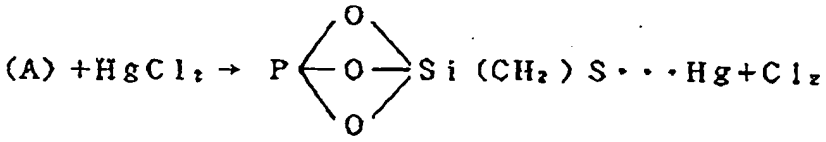
[Structure 2]



[0021]

(3) Removal of mercury compounds (such as $HgCl_2$) using said mercury removal agent A

[Structure 3]



[0022]

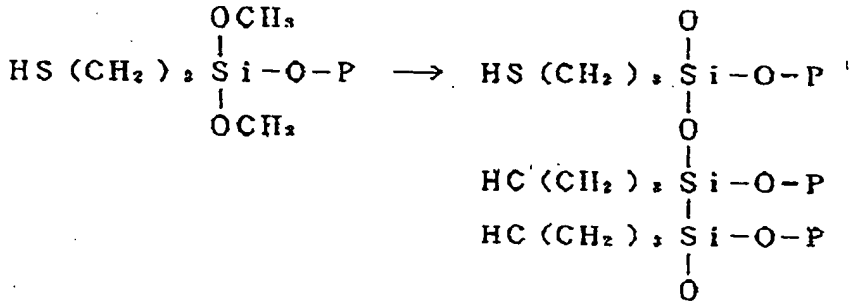
Because the reaction between inorganic powder (P) and mercury and the mercury compound in the flue gas is a solid-gas reaction (solid: solid mercury removal agent in the form of a dry powder or slurry; gas phase: mercury and mercury compound), it is necessary to use an

inorganic powder having a large specific surface area so as to promote the reaction. Inorganic powders having a large surface area usually have many surface hydroxyl groups. In addition, the inorganic powder usually has a high heat resistance and is stable in the temperature range of 150-230°C. Consequently, an inorganic powder is used as the support in this invention.

[0023]

Mercury is prone to reactions with sulfur compounds. Especially, mercapto groups (-SH groups) have excellent mercury adsorption capability. The silane coupling agent contains heat-resistant Si groups in it, and, when silane is hydrolyzed to form silanol (-Si-OH), condensation reaction with hydroxyl groups on the surface of the inorganic powder takes place to form siloxane bonds (-O-Si-O-). Consequently, it becomes chemically and thermally stable, and the heat resistance becomes higher.

[Structure 4]



[0024]

Consequently, the mercury removal agent prepared by reaction between the water-soluble silane coupling agent containing γ-mercapto groups and the inorganic powder has excellent heat resistance and mercury removal property.

[0025]

As explained above, the amount of the water-soluble silane coupling agent containing γ-mercapto groups with respect to the inorganic powder for reaction should be in the range of 0.1-5 wt%, or preferably in the range of 0.1-1 wt%. If the amount is too small, silane cannot be introduced into the inorganic powder sufficiently, so that the performance of removing mercury and mercury compounds will decrease. On the other hand, if the amount is too large, the cost will be high, and the inorganic powder as a support will be poisoned so that the solid-gas reaction is hampered. As a result, the performance of removing mercury and mercury compounds will decrease.

[0026]

Application examples

Application Example 1

First of all, an application example of the method for manufacturing the mercury removal agent of this invention will be explained.

[0027]

Example of manufacturing of mercury removal agent

20 g of silane liquid were added to 50 mL of ethyl alcohol, and the mixture was agitated to form a liquid A. Acetic acid was added to 1 L of water while stirring until the pH reached 4, to form liquid B. Liquid A was gradually added to liquid B to silanolate the silane. In this case, at first, the liquid was turbid. After agitation for 15-30 min, the liquid became transparent. This liquid was designated as liquid C.

[0028]

On the other hand, 1 kg of an inorganic powder was added to 4 L of water, and the mixture was agitated to form liquid D. While liquid D was agitated, said liquid C was gradually added. As needed, 10 mL of N-propylamine liquid were added as a reaction accelerating agent, and the mixture was agitated.

[0029]

After agitation at room temperature for 1 h, agitation was stopped, and a slurry mercury removal agent was obtained that can be used in the semidry method.

[0030]

In another method, the slurry mercury removal agent prepared above was allowed to stand still. The supernatant was discarded, and the precipitate was filtered. After the precipitate was washed with a small amount of ethanol, it was dried in the air. The dry product was crushed to form a powder of mercury removal agent that can be used in the dry method.

[0031]

(Mercury removal test)

Under the conditions listed in Table 2, 10 g of a mercury removal agent as a mixture of inorganic powder and silane coupling agent having γ-mercapto groups as listed in Table 1 were filled in a fused silica glass reaction tube with inner diameter of 40 mm and length of 750 mm.

Then, a simulated flue gas of a trash incinerator was fed through it, with results listed in Table 1. It can be seen that up to 72% of mercury can be removed.

Table 1

⑨試験No.	⑩無機粉体	無機粉体⑪重量部	カップリング剤⑫	カップリング剤⑬重量部	水銀除去率(%)⑭
①	二酸化珪素	100	①注)⑮	1	72
②	活性白土	〃	〃	〃	67
③	シリカゲル	〃	〃	〃	60
④	二酸化チタン	〃	〃	〃	70
⑤	モレキュラシーブ	〃	〃	〃	69
⑥	二酸化珪素	〃	〃	5	66
⑦	〃	〃	②注)⑯	1	63
⑧	活性白土	〃	〃	〃	58

⑰注) ①はγ－メルカプトプロピルトリヒドロキシシラン、
②はγ－メルカプトプロピルメチルジヒドロキシシラン

Key:
1 Silicon dioxide
2 Active terra alba
3 Silica gel
4 Titanium dioxide
5 Molecular sieve
6 Silicon dioxide
7 Same as above
8 Active terra alba
9 Test No.
10 Inorganic powder
11 Amount of inorganic powder, parts by weight
12 Coupling agent
13 Amount of coupling agent, parts by weight
14 Mercury removal rate (%)
15 Note [1]
16 Note [2]
17 Notes: [1] γ-mercaptopropyltrihydroxysilane
[2] γ-mercaptopropylmethyldihydroxysilane

Table 2

① 炉内温度	200℃
② ガスの線速度	1.0m/min.
③ Hg濃度	0.5mg/Nm³
④ HCl濃度	850ppm
⑤ SOx濃度	150ppm
⑥ O_2 濃度	10%
⑦ 水分濃度	26%
⑧ 除去剤充填量	10g
⑨ 通気時間	2時間⑩

Key: 1 Oven temperature
2 Linear velocity of gas
3 Hg concentration
4 HCl concentration
5 SO_x concentration
6 O_2 concentration
7 Moisture concentration
8 Amount of removal agent filled
9 Gas feeding time
10 2 h

[0032]

Application Example 2

Using the same method as in Application Example 1, except that diatomaceous earth or a mixture of diatomaceous earth and pearlite was used as the inorganic powder, and γ-mercaptopropyltrihydróxysilane was used as the silane coupling agent having γ-mercapto groups, with the amount of the latter being 1 part by weight with respect to 100 parts by weight of the former, the mercury removal agent listed in Table 3 was manufactured.

[0033]

Under the same conditions as those in Table 2 of Application Example 1, the mercury removal agent was filled in the fused silica glass tube for testing to determine the mercury removal effect. The results are listed in Table 3. In this case, the mercury removal rate is up to 85%.

Table 3

試 験 ① No.	ケイソウ土 ② (重量部)	パーライト ③ (重量部)	水銀除去率 ④ (%)
9	10	0	70
10	9	1	85
11	8	2	80
12	7	3	74
13	6	4	62
14	5	5	63

Key: 1 Test No.
2 Diatomaceous earth (parts by weight)
3 Pearlite (parts by weight)
4 Mercury removal rate (%)

[0034]

In the above, examples of the dry method have been explained. Similar effects can be realized when the mercury removal agent of this invention is used in a slurry or semidry form.

[0035]

Effect of the invention

This invention provides a type of mercury removal agent with excellent performance in the dry and semidry [mercury removal] methods, and its manufacturing method.